GB2162172

Publication Title:

Process for the production of ethanol

Abstract:

Abstract of GB2162172

A process for the production of ethanol comprises: (a) producing first and second streams of synthesis gas, each containing H2, CO and CO2; (b) separating CO2 from the first synthesis gas stream to give a CO2-rich gas and a CO2-depleted gas; (c) incorporating resulting CO2-rich gas into the second synthesis gas stream to give a synthesis gas of enriched carbon content; (d) passing resulting synthesis gas of enriched carbon content as make-up gas to a methanol synthesis plant containing a charge of a methanol synthesis catalyst and maintained under methanol synthesis conditions; (e) converting methanol from step (d) in one or more stages, including a carbonylation stage, into an alkyl acetate; (f) separating CO2-depleted gas of step (b) to form a CO-rich gas and an H-rich gas; (g) passing CO-rich gas from step (f) to the carbonylation stage of step (e); (h) subjecting alkyl acetate from step (e) to hydrogenolysis by reaction with H2-rich gas of step (f), in the presence of a hydrogenolysis catalyst maintained under hydrogenolysis conditions; (i) recovering product ethanol; and (j) recycling to step (e) an alkyl alcohol. t Data supplied from the esp@cenet database - Worldwide

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C2C

(54) **Process for the production of ethanol**

(57) A process for the production of ethanol comprises:

(a) producing first and second streams of synthesis gas, each containing H_2, CO and CO_2;

(b) separating CO_2 from the first synthesis gas stream to give a CO_2-rich gas and a CO_2-depleted gas;

(c) incorporating resulting CO_2-rich gas into the second synthesis gas stream to give a synthesis gas of enriched carbon content;

(d) passing resulting synthesis gas of enriched carbon content as make-up gas to a methanol synthesis plant containing a charge of a methanol synthesis catalyst and maintained under methanol synthesis conditions;

(e) converting methanol from step (d) in one or more stages, including a carbonylation stage, into an alkyl acetate;

(f) separating CO_2-depleted gas of step (b) to form a CO-rich gas and an H.rich gas;

(g) passing CO-rich gas from step (f) to the carbonylation stage of step (e);

(h) subjecting alkyl acetate from step (e) to hydrogenolysis by reaction with H_2-rich gas of step (f), in the presence of a hydrogenolysis catalyst maintained under hydrogenolysis conditions;

(i) recovering product ethanol; and
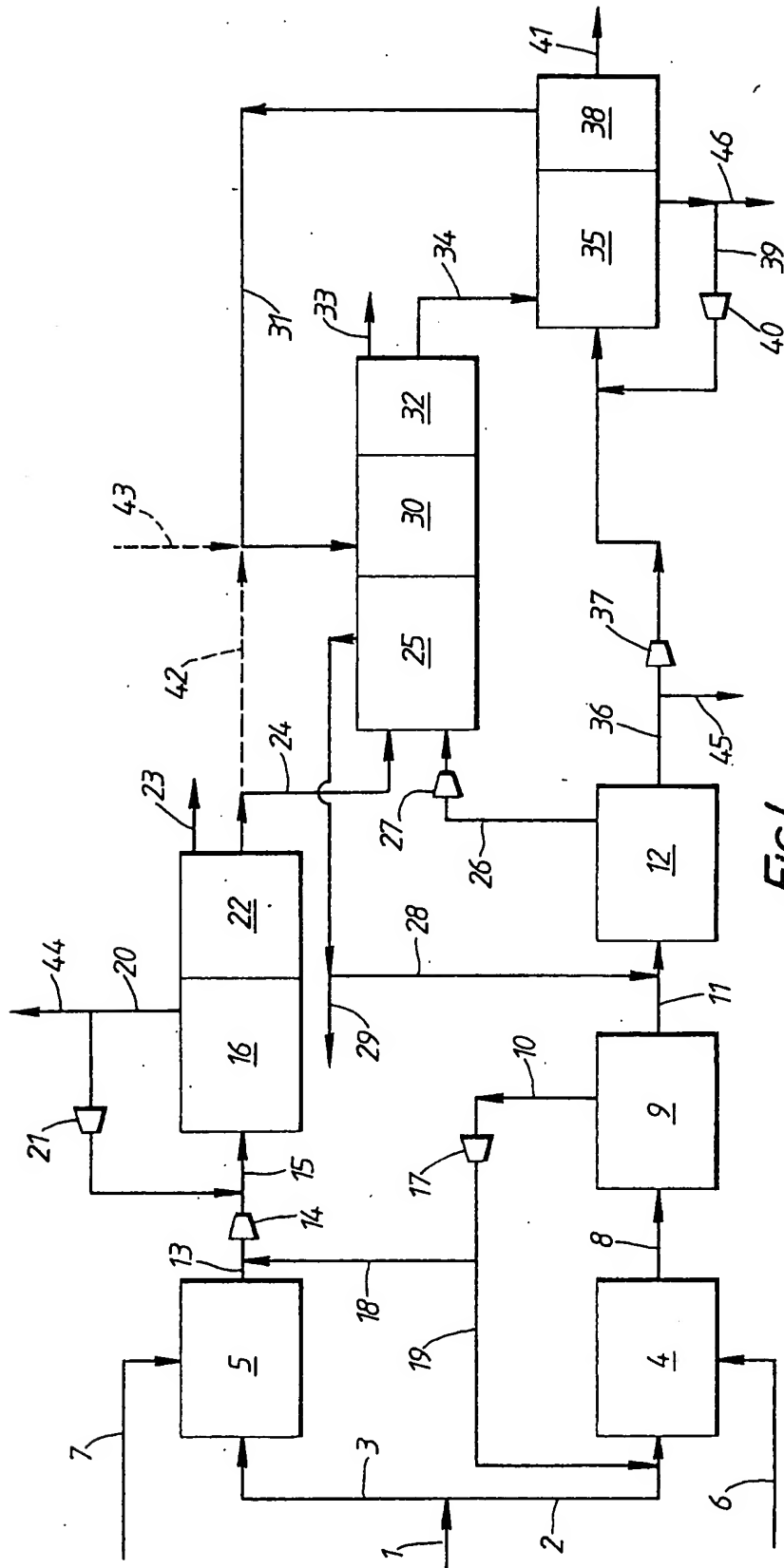
(j) recycling to step (e) an alkyl alcohol.

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Fig.1.

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Fig.2.

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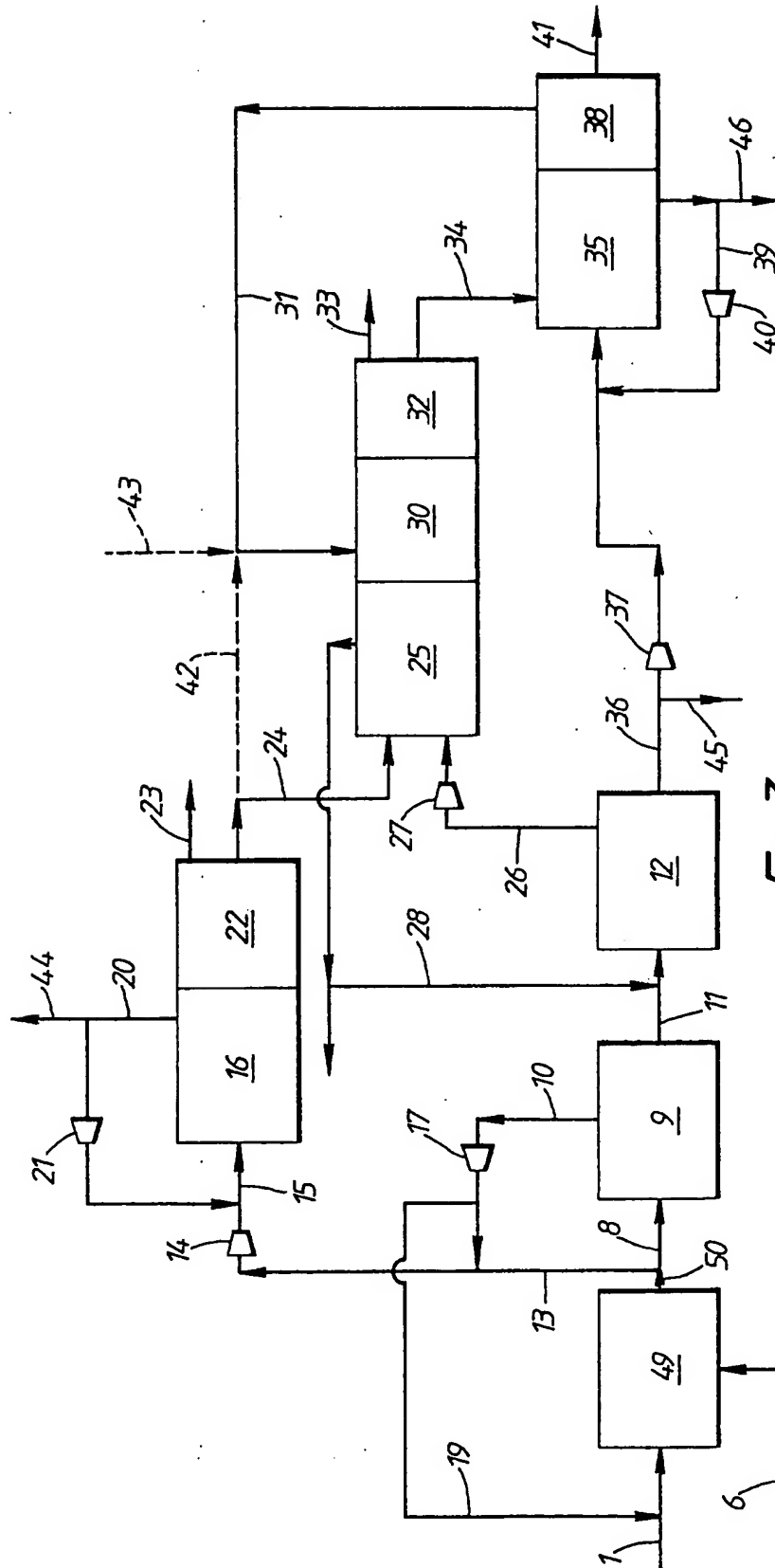Fig. 3.

SPECIFICATION

Process

5   This invention relates to a process for the produc-
tion of ethanol.
International Patent Publication No. WO83/03409
describes a process for for the production of
ethanol in which methanol is carbonylated by reac-
10 tion with carbon monoxide in the presence of a
suitable carbonylation catalyst, typically a nickel-or
rhodium-based carbonylation catalyst, to form an
acetic acid which is then esterified to give an acetic
ester which is, in turn, subjected to hydrogenolysis
15 in the vapour phase using, as hydrogenolysis cata-
lyst, a catalyst comprising a reduced mixture of
copper and zinc oxides. In the plant of Figure 1 of
that prior proposal a synthesis gas plant 1 is ar-
ranged to supply a synthesis gas, desirably an ap-
20 proximately 2:1 H_2:CO molar mixture, to methanol
synthesis plant 3 and also to provide the CO re-
quired for carbonylation of methanol in carbonyla-
tion stage 5. Hydrogen for hydrogenolysis of ethyl
acetate in zone 8 is supplied by way of line 7 as an
25 off gas from the carbonylation stage 5. Figure 2 il-
lustrates a plant in which synthesis gas is fed in
line 111 to ester hydrogenolysis zone 109; the
same synthesis gas plant can supply the methanol
synthesis plant (not shown) used to produce the
30 methanol supplied in line 101. In the plant of Fig-
ure 3 a synthesis gas plant supplies synthesis gas
both to the methanol synthesis plant 205 and also
to the ester hydrogenolysis zone 211.
In a methanol synthesis plant hydrogen and car-
35 bon oxides react together at elevated temperature
and pressure in the presence of a methanol syn-
thesis catalyst. The major reactions occurring are:

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

40

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O.$$
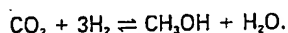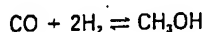
Hence the presence of CO_2 in the synthesis gas
is not disadvantageous. For optimum operation of
45 the methanol synthesis plant it is best to supply as
make-up gas a stoichiometric mixture of H_2, CO
and CO_2 of the following composition:

$$xCO + y\,CO_2 + (2x + 3y)H_2,$$
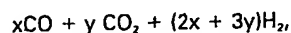
50
where x and y are integers. In practice the compo-
sition of a synthesis gas depends upon the feed-
stock and the process used and may vary
considerably. Thus a typcial dry gas composition
55 obtained by steam reforming of natural gas may
have the following composition: CO 15.5%, H_2
75.7%, CO_2 8.1%, N_2 + A 0.2%, CH_4 0.5%. On the
other hand partial oxidation of a heavy fuel oil may
yield a gas of the composition: CO 47.3%, H_2
60 46.7%, CO_2 4.3%. N_2 + A 1.4%, CH_4 0.3%. Although
the composition of the synthesis gas may be ad-
justed by use of the water gas shift reaction, i.e.:

$$CO + H_2O \rightleftharpoons CO_2 + H_2,$$

65
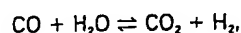
by absorption of CO_2 in a solvent liquor, such as
hot potassium carbonate or an amine wash liquor
(e.g. monoethanolamine or diethanolamine), or by
adsorption of H_2 using the so-called pressure
70 swing technique, it is often difficult, if not impossi-
ble, to achieve the desired stoichiometric synthesis
gas without having effectively to discard either H_2
or carbon in the form of CO_2. This has the result of
decreasing the overall efficiency of conversion of
75 the synthesis gas feedstock to methanol.
Similarly, the optimum efficiency of operation of
the methanol carbonylation plant it is best to use
substantially pure CO and it is also best to operate
the ester hydrogenolysis step using substantially
80 pure H_2. Again, although separate CO and H_2
streams can be produced from a synthesis gas by
CO_2 removal followed by dehydration and then CO/
H_2 separation, for example by the so-called "Co-
sorb" process, this sequence of steps results in
85 loss of CO_2 in the CO_2 removal step. Moreover, the
carbon oxides and H_2 may not be available in the
desired molar ratio so that one or other compo-
nent of the synthesis gas may have to be wasted,
thus increasing feedstock usage.
90 These losses inevitably increase the cost of pro-
ducing ethanol by this route.
It would accordingly be desirable to improve the
process efficiency of this route to synthetic
ethanol.
95 The present invention accordingly seeks to pro-
vide an improved ethanol synthesis process in
which the components of a synthesis gas are used
to optimum advantage so as to improve corre-
spondingly the yield of ethanol from a given quan-
100 tity of synthesis gas feedstock and to reduce its
cost of production.
According to the present invention there is pro-
vided a process for the production of ethanol
which comprises:
105   (a) producing first and second streams of syn-
thesis gas, each containing H_2, CO, CO_2;
(b) separating CO_2 from the first synthesis gas
stream to give a CO_2-rich gas and a CO_2-depleted
gas;
110   (c) incorporating resulting CO_2-rich gas into the
second synthesis gas stream to give a synthesis
gas of enriched carbon content;
(d) passing resulting synthesis gas of enriched
carbon content as make-up gas to a methanol syn-
115 thesis plant containing a charge of a methanol syn-
thesis catalyst and maintained under methanol
synthesis conditions;
(e) converting methanol from step (d) in one or
more stages, including a carbonylation stage, into
120 an alkyl acetate;
(f) separating CO_2-depleted gas of step (b) to
form a CO-rich gas and an H_2-rich gas;
(g) passing CO-rich gas of step (f) to the car-
bonylation stage of step (e);
125   (h) subjecting alkyl acetate from step (e) to hy-
drogenolysis by reaction with H_2-rich gas of step (f)
in the presence of a hydrogenolysis catalyst main-
tained under hydrogenolysis conditions;
(i) recovering resulting ethanol; and
130   (j) recycling to step (e) an alkyl alcohol.

The first and second synthesis gas streams of step (a) can be produced by dividing the output gas stream from a single synthesis gas plant. Alternatively they can be produced in separate synthesis gas plants or in different sections of the same synthesis gas plant. Any known process for generation of synthesis gas can be used. For example, the synthesis gas can be generated by steam reforming of natural gas or light hydrocarbon fractions (e.g. naphtha), by partial oxidation of a wide range of hydrocarbons from light hydrocarbons (e.g. natural gas) through to heavy fuel oils, or by gasification of coal using air to oxygen and steam. When the synthesis gas is generated by steam reforming of natural gas, the principal reaction is

$$H_2O + CH_4 \rightleftharpoons CO + 3H_2.$$
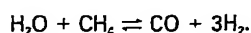
The resulting product mixture is in practice a mixture of H_2O, H_2, CO, CO_2 and CH_4 in dynamic equilibrium. Further description of the production of synthesis gas can be found, for example, in a survey article by J.H. Carvie, "Synthesis Gas Manufacture", Chemical and Process Engineering, November 1967, page 55 et seq.

The CO_2 separation step (b) preferably comprises contacting the first synthesis gas stream in a CO_2 absorption zone with a CO_2 absorption liquor, subjecting resulting CO_2 loaded liquor to CO_2 desorption conditions in a CO_2 desorption zone, and recovering resulting CO_2-rich gas. Typical CO_2 absorption liquors include hot alkaline liquors, such as those based on hot potassium carbonate, or on amines such as mono-and diethanolamine.

In step (c) of the process of the invention CO_2-rich gas from step (b) can be directly admixed with the second synthesis gas stream in order to enhance its carbon content. Alternatively, when the two synthesis gas streams are produced separately, either in separate plants or in different sections of the same plant, CO_2-rich gas from step (b) can be admixed with the carbonaceous feedstock, such as natural gas, used to generate the second synthesis gas stream; in this way the CO_2-rich gas is incorporated into the second synthesis gas stream upstream from the synthesis gas production step itself. Whichever method is adopted, the quantity of CO_2-rich gas thus incorporated into the second synthesis gas stream is desirably selected so as to yield a synthesis gas of enriched carbon content which has a composition which is approximately stoichiometric for methanol synthesis. In this way the methanol synthesis plant can be operated under optimum conditions with enhanced efficiency of usage of the carbon content of the carbonaceous feedstock used to form the second synthesis gas stream. This is particularly beneficial when using "carbon deficient" feedstocks, such as natural gas, to generate the synthesis gas for the second synthesis gas stream.

Any CO_2-rich gas from step (b) in excess of that required to form the synthesis gas of enriched carbon content of the second synthesis gas stream can be recycled to the steam reforming step which

is used to produce the first stream of synthesis gas. This has the benefit that the overall efficiency of use of carbon in the feedstock is maximised.

The methanol synthesis plant of step (d) can be of conventional design. Its design and operation do not form any part of the present invention. For a description of a typical methanol synthesis plant reference should be made to a paper by J.B. Horsley, P.L. Rogerson and R.H. Scott entitled "The Design and Performance of the ICI 100 atmosphere Methanol Plant", A. I. Chem. E., 74th National Meeting, March 11-15, 1973, New Orleans.

In step (e) of the process of the invention methanol is converted by a procedure involving one or more steps, including a carbonylation step, to form an alkyl acetate. Carbonylation of methanol has been described on many occasions and the reaction products usually include both acetic acid and methyl acetate. If the chosen carbonylation procedure yields methyl acetate as a major product, this can be passed on to the hydrogenolysis step and any acetic acid produced as by-product can either be recycled to the carbonylation step or can be esterified to give methyl acetate, or another alkyl acetate, which can also be passed forward for hydrogenolysis. On the other hand, it is alternatively possible to select in step (e) a carbonylation procedure that yields acetic acid as a major product, with possibly one a minor amount of methyl acetate as a by-product. In this case the acetic acid formed can be esterified with methanol, or with another alkyl alcohol, to form in a second step an alkyl acetate for use in the hydrogenolysis step (h) of the process of the invention. Any methyl acetate by-product from the carbonylation step can be passed also to the hydrogenolysis step (h).

As examples of descriptions of the carbonylation of methanol there can be mentioned GB-A-628509, GB-A-1233121, GB-A-1277242, GB-A-2089803, US-A-4134912 and US-A-4356320.

In the case that conversion of methanol to an alkyl acetate in step (e) of the process of the invention proceeds in two stages, with acetic acid being formed as an intermediate product, the alkyl alcohol is preferably methanol or ethanol so that the alkyl acetate is methyl or ethyl acetate. However it is also possible to use a C_{1}. alkanol having, for example, up to about 8 carbon atoms. Thus the alkyl alcohol may also be selected from n-propanol, i-propanol, n-butanol, sec-butanol, n-amyl alcohol, iso-amyl alcohol, n-hexanol, and 2-ethylhexanol whereupon the alkyl acetate corresponds to the alkyl alcohol selected.

Esterification can be conducted in known manner, typically by reaction of acetic acid with ethanol or another alkyl alcohol in the liquid or vapour phase in the presence of a suitable, typically acidic, esterification catalyst at normal or elevated temperature and under normal, elevated or reduced pressure.

Separation of CO and H_2 in step (f) of the process of the invention can also be carried out in conventional manner. Typical techniques include absorption of CO in a copper-containing liquor (the so-called "Cosorb" process), methane wash cry-

ogenic procedures, and pressure swing adsorption using molecular sieves. Again, the precise design of the CO/H₂ separation equipment and operating conditions to be used therein form no part of the 5 present invention.

Hydrogenolysis in step (h) can be effected in known manner. Although conventional liquid phase, high pressure processes can be used, in which the catalyst is, for example, a copper chrom-
10 ite or barium promoted copper chromite catalyst, it is preferred to utilise the vapour phase process described in International Patent Publication No. WO82/03854. This describes use of a catalyst comprising a reduced mixture of copper oxide and zinc
15 oxide at a temperature in the range of from about 75°C to about 300°C and at a pressure in the range of from about 0.1 bar to about 100 bar. Preferred reaction conditions include use of, for example, a pressure of from about 3 bar to about 60 bar, e.g.
20 about 5 bar to about 50 bar, and a tempeature of from about 150°C to about 250°C, e.g. about 180°C to about 240°C. In such a hydrogenolysis step the vapour pressure of the alkyl acetate preferably ranges from about 0.05 bar up to about 10 bar.
25 Preferably the hydrogenolysis step is conducted in the presence of excess hydrogen. Thus the hydrogen:alkyl acetate molar ratio may lie in the range of from about 2:1 up to about 100:1 or more.

Hydrogenolysis of each mole of alkyl acetate
30 yields, in the case of ethyl acetate, 2 moles of ethanol or, in the case of methyl acetate or another alkyl acetate, 1 mole of ethanol and 1 mole of methanol or the corresponding alkyl alcohol. In the former case approximately 1 mole of ethanol is re-
35 covered and passed forward for product recovery, whilst the remainder is recycled for esterification of further acetic acid. In the latter case, the alcohol mixture is separated, the ethanol being passed forward for product recovery whilst the other alkyl al-
40 cohol is recycled to esterification. Alternatively, if a single stage carbonylation procedure is used to produce methyl acetate, then the methanol recovered from the hydrogenolysis step can be recycled for further carbonylation. When methyl or
45 ethyl acetate is selected as the ester for hydrogenolysis, any make up quantities of methanol or ethanol required for alkyl acetate production can be produced within the plant itself. When another alkyl acetate is selected, it may be necessary to im-
50 port from beyond battery limits any make up alkyl alcohol required.

In order that the invention may be clearly understood and readily carried into effect, three forms of ethanol synthesis plant, each designed to operate
55 according to a preferred process in accordance with the invention, will now be described, by way of example only, with reference to Figures 1 to 3 of the accompanying drawings, each of which is a flow diagram of a respective form of plant.
60   Referring to *Figure 1* of the drawings, natural gas from line 1 is supplied by way of lines 2, 3 to steam reformer sections 4, 5 of conventional design. These reformer sections 4, 5 may comprise separate steam reformer furnaces or may comprise
65 different sections of the same steam reformer fur-

nace. Steam is supplied by way of lines 6,7 to each of the steam reformer sections 4,5.

From steam reformer section 4 there issues in line 8 a first synthesis gas stream containing typi-
70 cally 15.5% CO, 75.7% H₂, 8.1% CO₂, 0.2% (N₂ + A), and 0.5% CH₄. This is passed to a conventional CO₂ recovery zone 9 which is arranged to absorb CO₂ in a suitable liquor, such as activated potassium carbonate or an alkanolamine, from which the CO₂ is
75 subsequently desorbed by pressure reduction and heating in a desorption zone, the absorbent solution thereby regenerated being recycled for further absorption. The CO₂ separated from the first synthesis gas stream is recovered from zone 9 in line
80 10, whilst the residual gas mixture, which now largely consists of CO and H₂, is passed on in line 11 to a CO/H₂ separation zone 12.

A second synthesis gas stream of a similar composition to that of the first stream is produced in
85 reformer section 5 and exists therefrom in line 13. It is then compressed by means of compressor 14 to a pressure suitable for methanol synthesis, e.g. about 50 bar to 200 bar, and passes on in line 15 to a methanol synthesis plant 16.
90   The CO₂ recovered in line 10 is compressed by means of compressor 17; a part is passed by way of line 18 and is admixed with the second synthesis gas stream in line 13, whilst any CO₂ surplus to the methanol synthesis requirements is recycled to
95 the inlet of reformer section 4 in line 19. The proportion of CO₂ in line 10 that is passed through line 18 is preferably selected so as to produce a stoichiometric or near stoichiometric mixture of H₂, CO and CO₂ for methanol synthesis, e.g. a mixture
100 containing 70.9% H₂, 14.5% CO, 13.9% CO₂, 0.2% (N₂+A), and 0.5% CH₄.

Methanol synthesis plant 16 contains a conventional "low pressure" methanol synthesis catalyst, such as, for example, "ICI 51-2" catalyst manufac-
105 tured by ICI Limited. It is operated under conventional conditions, e.g. about 50 bar to about 200 bar at a temperature of from about 200°C to about 300°C. Methanol synthesis occurs by the following reactions:
110

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O.$$
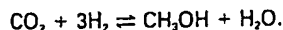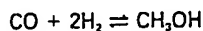
115 The crude product is separated from unreacted gas which is recycled in line 20 using recycle gas compressor 21, and is passed to a refining plant 22 of conventional design, water produced as byproduct being discarded in line 23, whilst pure methanol is
120 passed in line 24 to an acetic acid synthesis plant 25.

In acetic acid synthesis plant 25 methanol is carbonylated by reaction with carbon monoxide which is supplied from CO/H₂ separation plant 12 in line
125 26 with the aid of compressor 27. This reaction can be carried out using a suitable nickel-or rhodium-based carbonylation catalyst. Typical rhodium-based catalysts and relevant operating conditions therefor are described, for example, in GB-A-
130 1233121 and GB-A-1277242, whilst typical nickel

carbonylation catalysts and relevant operating conditions are described, for example, in US-A-4134912, US-A-4356320 and GB-A-2089803. A CO-containing purge gas is recycled in line 28 and is
5 mixed with the gas in line 11. Part or all of this purge gas can, if desired, be taken in line 29 for use, for example, as fuel in one of the steam reformer sections 4 and 5.

Acetic acid from plant 25 is then esterified in es-
10 terification section 30 with an alcohol, such as ethanol, supplied in line 31. Esterification section 30 can be operated using conventional techniques. For example, esterification can be carried out in the liquid phase by contacting a mixture of ethanol
15 or other alkyl alcohol and acetic acid with a conventional esterification catalyst such as sulphuric acid or an acidic ion exchange resin. Such a liquid phase esterification process can be conducted at elevated temperature, e.g. at the boiling point of
20 the mixture, at normal or elevated pressure and the ester recovered by distillation in a refining zone 32. Alternatively esterification may be carried out as a vapour phase process by passing a mixture of acetic acid and ethanol, or another alcohol, at nor-
25 mal or elevated pressure and appropriate temperature over a suitable acidic catalyst, such as silica gel, activated charcoal, potassium hydrogen sulphate, phosphoric acid-treated coal, calcium phosphate, or an acidic ion exchange resin. In such a
30 vapour phase process an inert carrier gas may be included in the esterification mixture. In the esterification step it is preferred to use an approximately stoichiometric mixture of acetic acid and alcohol, e.g. ethanol. However it is also possible to operate
35 with either the acid or the alcohol in excess.

In refining zone 32 the water formed during the esterification reaction is separated by distillation in one or more stages from alkyl acetate and any unreacted acetic acid and/or alkyl alcohol. If the ester
40 forms an azeotrope with water and/or the alkyl alcohol, then this azeotrope is broken and separated in conventional manner. The water formed in the esterification reaction is recovered in line 33, whilst the ester, now essentially free from water, passes
45 on in line 34. Untreated alkyl alcohol (e.g. ethanol) and/or acetic acid is or are recycled internally to the esterification zone.

Alkyl acetate (e.g. ethyl acetate) in line 34 is fed to a vapour phase hydrogenolysis zone 35, to
50 which is also fed the H_2-rich stream in line 36 from CO/H_2 separation plant 11. This H_2-rich stream is first compressed using compressor 37.

CO/H_2 separation plant 12 may be, for example, a pressure swing adsorption plant, a plant using the
55 so-called "Cosorb" process, or a methane wash cryogenic plant. A description of pressure swing adsorption is given in an article by J.L. Heck entitled "First U.S. Polybed PSA unit proves its reliability", Oil & Gas Journal, February 1980. The
60 "Cosorb" process and the methane wash cryogenic process are both described by K.W. Foo and I. Shortland in an article "Compare CO production methods", Hydrocarbon Processing, May 1976, pages 149 to 152. Another description of the "Co-
65 sorb" process can be found in "CO recovery and

purification" by Donald J. Haase, Paul M. Duke and John W. Cater, Hydrocarbon Processing, March 1982, pages 103 to 106.

Hydrogenolysis zone 35 uses the vapour phase
70 hydrogenolysis process described, for example in International Patent Publication No. WO82/03854. In this process a vaporous mixture of alkyl acetate (e.g. ethyl acetate) from line 34 and hydrogen rich gas from line 36 is contacted with a catalyst com-
75 prising a reduced mixture of copper oxide and zinc oxide, typically at a pressure of from about 5 bar to about 40 bar and at a temperature of from about 150°C to about 240°C. Usually it will be preferred to use an excess of hydrogen, i.e. in excess of the
80 two moles of hydrogen demanded by the stoichiometry of the hydrogenolysis reaction; e.g.:

$$CH_3.CO.O.CH_2.CH_3 + 2H_2 = 2CH_3.CH_2.OH.$$
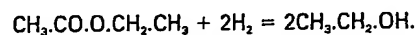
85 Thus the hydrogen:ester molar ratio in the vaporous mixture preferably is in excess of about 5:1 up to about 20:1 or more. Zone 35 can comprise a tubular or multi-tubular cooled reactor or a single bed or multi-bed adiabatic hydrogenolysis reactor
90 or reactors. At the downstream end of zone 35 the condensible components are separated from the gaseous components by condensation. the liquid condensate, which consists predominantly of ethanol, when the alkyl acetate is ethyl acetate, or
95 a mixture of ethanol and another alcohol such as methanol, if another alkyl acetate (e.g. methyl acetate) is used, is passed to a refining section 38 of conventional design, whilst excess hydrogen is recycled in line 39 by means of gas recycle compres-
100 sor 40. Ethanol product is recovered in line 41, whilst alkyl alcohol required for esterification of acetic acid in esterification section 30 (which is ethyl alcohol if the ester is ethyl acetate or another alcohol, e.g. methanol, if a different alkyl acetate,
105 such as methyl acetate, is used) is recycled in line 31, together with any unreacted alkyl acetate. If an alkyl alcohol other than ethyl alcohol is used, then any necessary make up alkyl alcohol is supplied via line 42 in the case of methanol (or via line 43 in
110 the case of a C_{3+} alkanol) and is admixed with the recycled material in line 31.

A purge stream to control the level of inert materials (e.g. methane) in the methanol synthesis loop is taken from line 20 by way of line 44 and used as
115 fuel. Any hydrogen in excess of that required for hydrogenolysis is recovered in line 45 for export beyond battery limits or for use as fuel, e.g. for the reformer sections 4, 5. The level of inert gases and/or excess hydrogen in the hydrogenolysis recycle
120 loop is controlled by taking a purge stream in line 46 for use as a fuel. Conveniently the purge streams in lines 44 and 46 are used in the steam reformer sections 4 and 5, thus reducing the amount of natural gas or other fuel required for
125 this purpose.

The plant of Figure 2 is generally similar to that of Figure 1 and accordingly the same reference numerals have been used to denote like parts to those present in the plant of Figure 1. In the plant
130 of Figure 2 line 18 is replaced by a line 47 so that

part of the CO_2 recovered in line 10 is admixed
with the natural gas feedstock supplied in line 3 to
steam reformer section 5. Hence part of the CO_2 re-
covered from the first synthesis gas stream is in-
5 corporated into the second synthesis gas stream in
line 13 upstream from the steam reformer section
5, whilst the remainder is recycled in line 19 to the
upstream end of steam reformer section 4. As with
the plant of Figure 1, the quantity of CO_2 passed by
10 way of line 47 is preferably sufficient to produce in
the second synthesis gas stream in line 13 the de-
sired $CO:CO_2H_2$ molar ratio that is stoichiometric,
or near stoichiometric, for methanol production.

Whereas a two step process is used in the plant
15 of Figure 1 to produce an alkyl acetate, such as
ethyl acetate, from methanol in line 24, carbonyla-
tion stage 25 and esterification section 30 of the
plant of Figure 1 are replaced by a single stage
methyl acetate production plant 48 in the plant of
20 Figure 2. Methyl acetate from refining zone 32 is
passed by line 34 to hydrogenolysis plant 35 whilst
methanol is separated from ethanol in refining sec-
tion 38 and recycled to the carbonylation step in
line 31.
25   The plant of Figure 3 is similar to that of Figure 1
except that, in Figure 3, a single synthesis gas
plant 49 replaces the two steam reformer sections
4 and 5 of the plant of Figure 1. The resulting syn-
thesis gas stream in line 50 is divided to give the
30 first and second synthesis gas streams in lines 8
and 13 respectively. Any CO_2-rich gas in line 10 in
excess of that required to give the approximately
stoichiometric mixture in line 13 required for meth-
anol synthesis is recycled in line 19 to the up-
35 stream end of reformer furnace 49.

CLAIMS

1. A process for the production of ethanol
40 which comprises:
   (a) producing first and second streams of syn-
thesis gas, each containing H_2, CO and CO_2;
   (b) separating CO_2 from the first synthesis gas
stream to give a CO_2-rich gas and a CO_2-depleted
45 gas;
   (c) incorporating resulting CO_2-rich gas into the
second synthesis gas stream to give a synthesis
gas of enriched carbon content;
   (d) passing resulting synthesis gas of enriched
50 carbon content as make-up gas to a methanol syn-
thesis plant containing a charge of a methanol syn-
thesis catalyst and maintained under methanol
synthesis conditions;
   (e) converting methanol from step (d) in one or
55 more stages, including a carbonylation stage, into
an alkyl acetate;
   (f) separating CO_2-depleted gas of step (b) to
form a CO-rich gas and an H_2-rich gas;
   (g) passing CO-rich gas from step (f) to the car-
60 bonylation stage of step (e);
   (h) subjecting alkyl acetate from step (e) to hy-
drogenolysis by reaction with H_2-rich gas of step
(f), in the presence of a hydrogenolysis catalyst
maintained under hydrogenolysis conditions;
65   (i) recovering product ethanol; and

(j) recycling to step (e) an alkyl alcohol.
   2. A process according to claim 1, in which the
alkyl acetate is ethyl acetate and the alkyl alcohol
recycled in step (j) is ethanol.
70   3. A process according to claim 1, in which the
alkyl acetate is methyl acetate and the alkyl alcohol
recycled in step (j) is methanol.
   4. A process according to claim 3, in which
methanol is carbonylated in step (e) to yield
75 methyl acetate directly.
   5. A process according to any one of claims 1
to 4, in which the CO_2 separation step (b) com-
prises contacting the first synthesis gas stream in a
CO_2 absorption zone with a CO_2 absorption liquor,
80 recovering resulting CO_2-depleted gas stream, sub-
jecting resulting CO_2-loaded liquor to CO_2 desorp-
tion conditions in a CO_2 desorption zone, and
recovering resulting CO_2-rich gas.
   6. A process according to any one of claims 1
85 to 5, in which the synthesis gas of enriched carbon
content of step (c) has a composition which is ap-
proximately stoichiometric for methanol synthesis.
   7. A process according to claim 6, in which the
first synthesis gas stream is produced by steam re-
90 forming of natural gas and CO_2-rich gas in excess
of that required to form the synthesis gas of en-
riched carbon content is recycled to the steam re-
forming step.
   8. A process according to any one of claims 1
95 to 7, in which hydrogenolysis is effected in step (h)
by contacting a vaporous mixture comprising alkyl
acetate and hydrogen with a catalyst comprising a
reduced mixture of copper oxide and zinc oxide at
a temperature in the range of from about 75°C to
100 about 300°C and at a pressure in the range of from
about 0.1 bar to about 100 bar.
   9. A process for the production of ethanol con-
ducted substantially as herein described with par-
ticular reference to any one of Figures 1 to 3 of the
105 accompanying drawings.